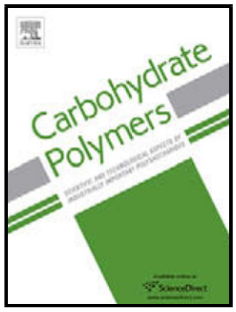

Title: Study of the behavior of biodegradable starch/polyvinyl alcohol/rosin blends

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Study of the behavior of biodegradable starch/polyvinyl alcohol/rosin blends

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Highlights:

- -Biodegradable potato starch/PVA/rosin blends were developed.
- -Addition of rosin to the blends improves mechanical properties substantially.
- -Mechanical properties are comparable to those offered by polymers such as LDPE.
- -Starch/PVA/rosin blends could be interesting materials for packaging applications.

Abstract

Biodegradable potato starch/PVA samples containing different concentrations of rosin were prepared by melt-mixing in order to study the enhancement of the properties of native starch films. Glycerol and polyvinyl alcohol (PVA) are commonly used as plasticizers of starch. Their relatively low molecular weight (compared with starch) contributes to a good processability. Rosin is a renewable product whose incorporation in the starch/PVA matrix induces processing aid and reinforcing effects. Its relatively high molecular weight might prevent its migration to the surface of the final product. Water content, solubility in water, mechanical properties, microstructure and dynamic mechanical analysis of the samples were studied. The addition of 8% rosin to starch/PVA blends led to tensile strength values higher than 10 MPa and elongation at break values close to 2000%, values comparable to those offered by conventional polymers used in

food packaging, for example LDPE. Furthermore, starch compounds have low cost and high biodegradability.

Keywords: Potato starch; polyvinyl alcohol; rosin; melt mixing; polymer blend.

1. Introduction

The extensive use of petroleum-based synthetic polymers for the packaging industry in recent decades has brought with it severe pollution problems. Increased environmental concerns and the fact that petroleum reservoirs are being dramatically reduced have led to a search for new alternatives to the non-biodegradable and non-renewable polymers used at present (Aydin & Ilberg, 2016; Cano et al., 2015). Bioplastics obtained from biopolymers such as starch, cellulose, lignin, chitin, etc. are renewable, environmentally-friendly and biodegradable materials, whose use contributes to the reduction of waste and to a more sustainable ecosystem (Tian et al., 2017).

Starch is a polymeric carbohydrate composed of two major biomacromolecules: amylose (mainly linear) and amylopectin (hyper-branched) (Xie et al., 2014). It is used by nature as a way to store energy in cereals, tubers and legumes. Starch is considered as one of the most promising options for replacing petrochemical polymers mainly due to its wide availability and low cost (Souza et al., 2012). Nevertheless, starch-based plastics have a major drawback, their fast aging and retrogradation of starch, which makes difficult their use in long-term applications (Malmir et al., 2018; Thakur et al., 2018; Zhu et al., 2012). Starch retrogradation is the responsible of the reorganization of gelatinized amylose and amylopectin chains in new and different ordered structures (Wang et al., 2015; Jiménez et al., 2012). Retrogadation is an ongoing process, which initially involves the rapid recrystallization of amylose molecules followed by the slow recrystallization of amylopectin molecules (Wang et al., 2015). Starch retrogadation is usually accompanied by physical changes in the films, as for example the migration of water and other

plasticizers and a relevant increase in the degree of crystallinity, processes that may involve significant changes of their mechanical properties with time and hence a marked starch samples instability (Zhang & Rempel, 2012; Wittaya, 2012; Morales et al., 2015). In addition, the lack of tensile strength of starch-based films is also remarkable and is limiting their applications in materials engineering (Tian et al., 2017).

Among all types of starch, potato starch represents 14% of the starch produced in Europe (Waterschoot et al., 2015) and 4% in the world (Basiak et al., 2017). Potato starch is a very refined starch, which contains minimum quantities of proteins and lipids. Besides its lower cost, potato starch has a higher swelling power, solubility, paste clarity and viscosity than the starch obtained from other natural sources such as wheat, rice or corn (Teixeira et al., 2018).

The blending of starch with other biodegradable materials, such as polyvinyl alcohol (PVA), has been proposed as an alternative because it improves the properties of starch materials, has a relatively low cost, and can be used in food applications (Aydin & Ilberg, 2016; Tian et al., 2017). Although PVA is a synthetic polymer, it is easily degraded by biological organisms. During the last century, many applications were developed with PVA in different sectors, such as food and medicine, yielding products such as lacquers, resins, surgical threads and food packaging materials (Gaaz et al., 2015). PVA has a high degree of biocompatibility and notable physical properties due to its hydroxyl groups, which promote the formation of hydrogen bonds (Cano et al., 2015).

Starch-PVA films made with starch obtained from different sources by the casting solution technique have been widely studied (Cano et al., 2015; Aydin & Ilberg, 2016; Jayasekara et al., 2004; Ramaraj, 2007; Shi et al., 2008), even though this processing technique is highly inefficient and time-consuming. By contrast, melt processing under shear force conditions enables starch and PVA to be blended in an industrially scalable

process. Few studies involving the preparation of starch/PVA blends by melt-mixing can be found in the literature (Tian et al., 2017; Liu et al., 2016), and more studies are necessary as a prior step to the manufacture of starch/PVA blends for applications such as food packaging.

Rosin, also known as colophony, is a naturally occurring solid form of resin obtained from pines and other conifers. Rosin and its derivatives have been used as plasticizers of polylactic acid (Moustafa et al., 2017; Narayanan et al., 2017) and poly(butylene adipate-*co*-terephthalate) (Moustafa et al., 2017) due to their chemical structure with highly hydrogenated phenanthrene rings (Niu et al., 2018). They can also be used as reinforcing and co-antimicrobial agents in polylactic acid films (Niu et al., 2018). Among their properties should be mentioned their biocompatibility, biodegradability, non-toxicity, antimicrobial activity and film-forming and UV-light absorbing capabilities. All these properties make rosin a potential candidate to be used in food packaging materials (Narayanan et al., 2017; Niu et al., 2018).

The aim of the present work is the study of the behavior of potato starch/PVA/rosin blends obtained by melt mixing and compression molding for potential application in food packaging. Specifically, the effect of the rosin content on the composite's mechanical properties, thermo-mechanical behavior and morphology was evaluated using sheets with different proportions of rosin. To the best of our knowledge, this is the first time that rosin has been used in the literature for starch/PVA compounding.

2. Materials and methods

2.1. Materials

Potato starch was provided by Across Organics (Geel, Belgium). PVA (M_w: 125000) was purchased from Sigma-Aldrich (Madrid, Spain) and the plasticizer glycerol was supplied

by Fisher Chemical (Geel, Belgium). Rosin (CAS: 8050-09-07) was generously supplied by Ismael Quesada S.A. (Elche, Spain). Butylhydroxytoluene (BHT) and zinc stearate, used as antioxidant and lubricant respectively, were provided by Sigma-Aldrich (Madrid, Spain). All chemicals were used without further purification.

2.2. Sample preparation

Starch, PVA, water and glycerol were weighed and manually pre-mixed at room temperature for 3 min. The content of glycerol and water in the sample was fixed at 29.7 wt. % and 19.8 wt. %, respectively, and the solid materials, starch and PVA, represented 24.75 wt. % and 24.75 wt. %, respectively. Small amounts (0.5 wt. %) of BHT and zinc stearate were also added to all formulations. To this blank formulation different amounts of rosin were added in variable ratios in order to obtain 80 grams of the formulations employed in the present study (0, 1, 5, 8, 10, 12 and 15 wt. % of rosin on the basis of the blank formulation yielded the formulations labeled as R0, R1, R5, R8, R10, R12 and R15, respectively). Sample preparation was done following procedures for starch melt-compounding previously described in the literature (Róz et al. (2006); Tian et al. (2017)) with some modifications after their optimization with our equipment. The blends were processed at 110ºC in a HAAKE™ PolyLab™ QC Modular Torque Rheometer (ThermoFisher Scientific, Waltham, MA, USA) for 25 min at 100 rpm. Blends were hot pressed at 160 ºC at a pressure of 6 ton for 10 min into 1 mm thick plates. Then, the samples were cooled under pressure.

2.3. Samples Characterization

The samples were conditioned at 25ºC and relative humidity of 50% for a week before characterization. The 50% of relative humidity was obtained by placing the samples in a desiccator with saturated magnesium nitrate solution at room temperature as in Xie et al. (2014). Their thickness was measured with a Format digital IP54 micrometer (Madrid,

Spain) at different locations and the mean value was calculated. The thickness of the samples ranged from 0.9 to 1.1 mm.

2.3.1. Hydration properties

The water content and solubility in water of the samples was determined in 1 x 1 cm^2 specimens following the procedures described by Hornung et al. (2018) and Medina-Jaramillo et al. (2017) with some modifications. Firstly, the water content was measured by determining the loss of weight of the sheets after drying in an oven for 5 h at 110 ºC. The measurements were taken in quadruplicate. The quantity of absorbed water or moisture content (*H*) was expressed as a percentage (grams of water in 100 grams of sample) using Eq. (1).

$$H\ (\%) = \left(\frac{m_0 - m_1}{m_0}\right) \times 100 \qquad (1)$$

where m_0 and m_1 are the mass before and after drying, respectively.

After that, the solubility in water was measured by placing the above dried samples individually in 10 mL tubes filled with 9 mL of distilled water. The tubes were capped and stored at 25 ºC for 24 h, after which the samples were taken out and dried again at 110 ºC for 5 h in order to determine the final mass of dry matter, m_f. The solubility in water was calculated from the loss of total soluble matter as follows (Eq. 2):

$$Solubility\ (\%) = \left(\frac{m_0 - m_f}{m_0}\right) \times 100 \qquad (2)$$

Water solubility values were obtained from the average of at least four repetitions.

2.3.2. Mechanical properties

The mechanical properties of the sheets were determined with an Instron 3344 Universal Test instrument (MA, USA) equipped with 2000N load cell and operated at 25 mm/min following ASTM D882-12 (2012) standard recommendations as in previous works

(Hornung et al. (2018); Luchese et al. (2017); Edhirej et al. (2018); Phetwarotai et al. (2018); Medina Jaramillo et al. (2015); Lopez et al. (2014)). The samples were cut into dumbbell-shaped specimens. The mechanical properties of each sample sheet were calculated using the average thickness of the specimen and at least 8 specimens per sample. The tensile properties studied were tensile strength at break, percentage of elongation at break and Young's modulus.

2.3.3. Scanning Electron Microscopy (SEM) Analysis

The morphology of the sheets was observed by SEM images obtained with a Hitachi Scanning Electron Microscope (Hitachi S3000N, USA) using an accelerating voltage of 5 kV. Dry sheet samples were cryofractured by immersion in liquid nitrogen. Before analysis, the fractured section was coated with gold for better observation.

2.3.4. Dynamic Mechanical Analysis (DMA)

The DMA analysis was performed in a DMA 1 Instrument (Mettler-Toledo, Barcelona, Spain) working in single-cantilever mode in two types of experiment: i) frequency sweep (0.09-50 Hz) at constant temperature (100 ºC) and ii) temperature sweep (from -100 to 60 ºC at a rate of 3 ºC/min) at constant frequency (1 Hz) as in Malmir et al. (2018). The dimensions of the specimens used for the DMA were 8.5 x 25 x 1 mm.

3. Results and discussion

Visual observation of the plates obtained by hot-pressing showed that R0 samples were clear and transparent. The higher the rosin content, the lower the transparency while, at the same time, the material became gradually more yellowish.

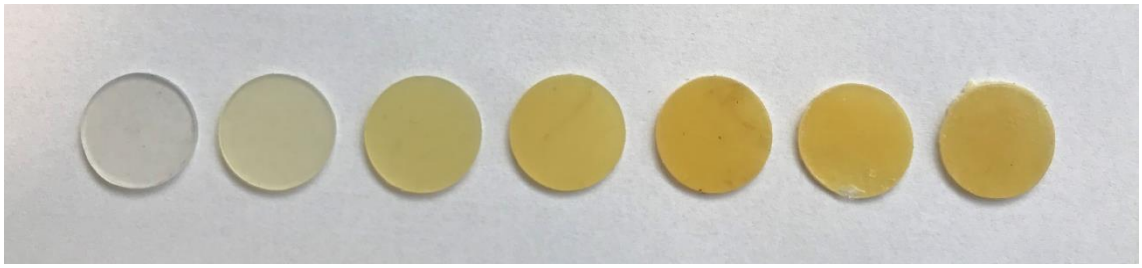

Figure 1. Visual appearance of the sheets obtained. From left to right: R0, R1, R5, R8, R10, R12 and R15 samples.

3.1. Hydration properties

Generally, the sensitivity of films to environmental conditions is a very important limiting factor (Bergo et al., 2013). As regards the application of films in food packaging, it is advisable to determine the water content of the sheets because starch sheets and food are hygroscopic. Both starch and PVA are multi-hydroxyl polymers with a hydrophilic character (Tian et al., 2017). In addition, water is a plasticizer of starch, and so the water molecules in sheets can change their physical properties (Lawton, 1996). The water content of the samples is shown in Table 1. As can be seen, sheets containing rosin showed a slightly decreasing water content until the rosin content was 10% (wt.). Values of the water content were similar or, in many cases, lower than those found in the literature for starch/PVA films (Cano et al., 2015; Ramaraj, 2007; Das et al., 2010). In addition, our values for the water content are considerably lower than those previously published for native starch films (López et al., 2011; Medina Jaramillo et al., 2015; Basiak et al., 2017). This could be an advantage of the developed starch/PVA blends compared with starch films and with other previously synthesized starch/PVA films maintaining the biodegradability of the material.

Table 1. Water content and solubility in water values of the sheets studied.

Sample	Water content (%)	Solubility in water (%)
R0	14.6 ± 0.2	41.9 ± 0.8

R1	5.3 ± 0.2	37.3 ± 0.7
R5	4.5 ± 0.3	35.9 ± 0.4
R8	3.3 ± 0.4	33.7 ± 0.3
R10	2.3 ± 0.8	32.7 ± 0.7
R12	4.0 ± 0.1	35.7 ± 0.8
R15	4.3 ± 0.6	34.7 ± 0.1

The solubility in water is a key parameter of biodegradable blends of a water-sensitive biopolymer such as starch, and a water-soluble polymer such as PVA. Indeed, water solubility is closely related to biodegradability (Medina Jaramillo et al., 2015). Water insolubility of the blends could be required for future applications as biodegradable packaging in order to ensure product integrity and water resistance (Basiak et al., 2017). However, for other applications such as the encapsulation of food or additives, partial solubility in water might be more suitable (Shen et al., 2010). The water solubility of the samples is also shown in Table 1. This parameter follows the same trend as the water content results. It is known that rosin is a hydrophobic material (Pathak & Dorle, 1990; Huang et al., 2015) because it is mostly composed of rosin acids (90%) whose structure is formed by a hydrophobic skeleton with hydrophilic carboxyl groups attached (Atta et al., 2006). Therefore, both parameters (water content and solubility in water) should decrease when the rosin content in blends increases. More specifically, these molecules provide fewer active sites in the starch/PVA matrix, in which the water molecules can be adsorbed. In fact, rosin-based sizing agents have traditionally been used in the paper industry to increase hydrophobicity (Huang et al., 2015). However, in our case a plateau was observed at a 10% (wt.) rosin content, pointing to a certain saturating effect. Similar values of solubility in water can be found in the literature for starch films (Medina Jaramillo et al., 2015).

3.2. Mechanical properties, SEM and Dynamic Mechanical Analysis

Mechanical properties can be influenced by the sample thickness, processing method, test speed, specimen shape, etc. (Souza et al., 2012) making a rigorous comparison with the results obtained by other researchers complicated.

Tensile strength-elongation curves were obtained for all the samples at room temperature. Figure 2 shows the mechanical properties of the starch/PVA blends studied with different rosin contents. As can be seen, standard deviations for elongation at break were higher than those obtained for the other magnitudes, which is in good agreement with the results reported by other researchers (Ferry & Morrison, 1944).

Maximum tensile strength varied from (4.6 ± 0.8) MPa to (10.7 ± 0.3) MPa. Figure 2a shows that the maximum tensile strength of the blends increased as the rosin content increased from 0 to 8% (wt.), reaching a maximum value at this concentration.

Similar behavior was observed for elongation at break (Figure 2b), which showed a maximum of (1987 ± 187) % at a rosin content of 8% (wt.). Young's Modulus in the different samples presented a minimum value above 8% rosin (Figure 2c), meaning that the sample becomes more elastic and hence less stiff.

These maxima at both tensile strength and elongation at break suggest that rosin at concentrations up to 8% forms a partially compatible blend with starch and PVA, rosin readily contributing to enhanced mechanical properties. However, the decrease in both properties in samples with a higher rosin content could be interpreted in terms of the segregation of a new phase poorly compatible with the blend. This hypothesis was investigated by two different techniques, SEM and DMA (see below).

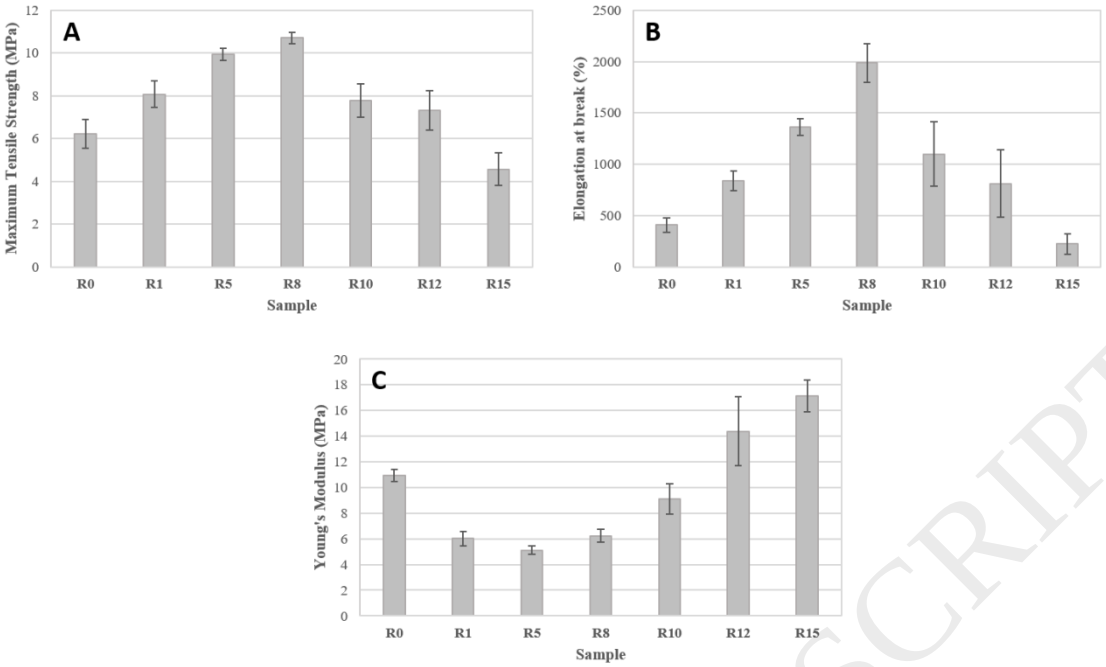

Figure 2. Mechanical properties of the starch/PVA blends studied. a) Maximum tensile strength; b) Elongation at break; c) Young's modulus.

As regards the mechanical properties, it was concluded that starch/PVA blends incorporating a medium content of rosin have tensile strength values higher than 10 MPa and elongation at break close to 2000 %, which is much better than that offered by common LDPE package films (Kormin et al., 2017).

In summary, each component of the blends (starch, PVA and rosin) not only contributes to the properties of the sample, but also modifies the starch-PVA and starch-rosin interactions which eventually influences the mechanical properties of the sheets. In this work, both polymers and rosin show good affinity and mutual property supplement, providing good tensile strength without sacrificing elongation of the samples.

Figure 3 shows the SEM images of the cross section of all the studied samples, where the presence of heterogeneous zones could be attributed to the amorphous nature of the blends. It can be observed that some particle domains appear, indicating phase separation.

It is known that the addition of starch to PVA decreases PVA crystallinity. Phase separation was also observed in starch/PVA blends by other authors (Tian et al., 2017; Cano et al., 2015; Sreekumar et al., 2012) as well as in pure thermoplastic starch systems, where it was attributed to the remains of starch granules that are still recognizable (called ghost granules). The ratio of these ghost granules in formulations with 0 and 1% rosin seems to be so low that they have no negative effect, since they exhibit both good transparency and acceptable mechanical strength, revealing that the blends behave as an apparent single-phase system. Indeed, in Figure 3, the presence of rosin grains is almost negligible in the sheets containing 1% rosin.

For higher rosin contents (above 5%), a new phase becomes prominent. This consists of spherical “droplets”, somewhat deformed in some cases (Figures 3c, 3d, 3e, 3f and 3g), that become more noticeable with the rosin content increases. It is worth mentioning that this new phase seems to show good miscibility or adhesion to the continuous phase in the sense that they seem closely joined. Nevertheless, at concentrations of 10 and 12% (coinciding with a drop in the mechanical properties) some cracks and a lack of cohesion is observable.

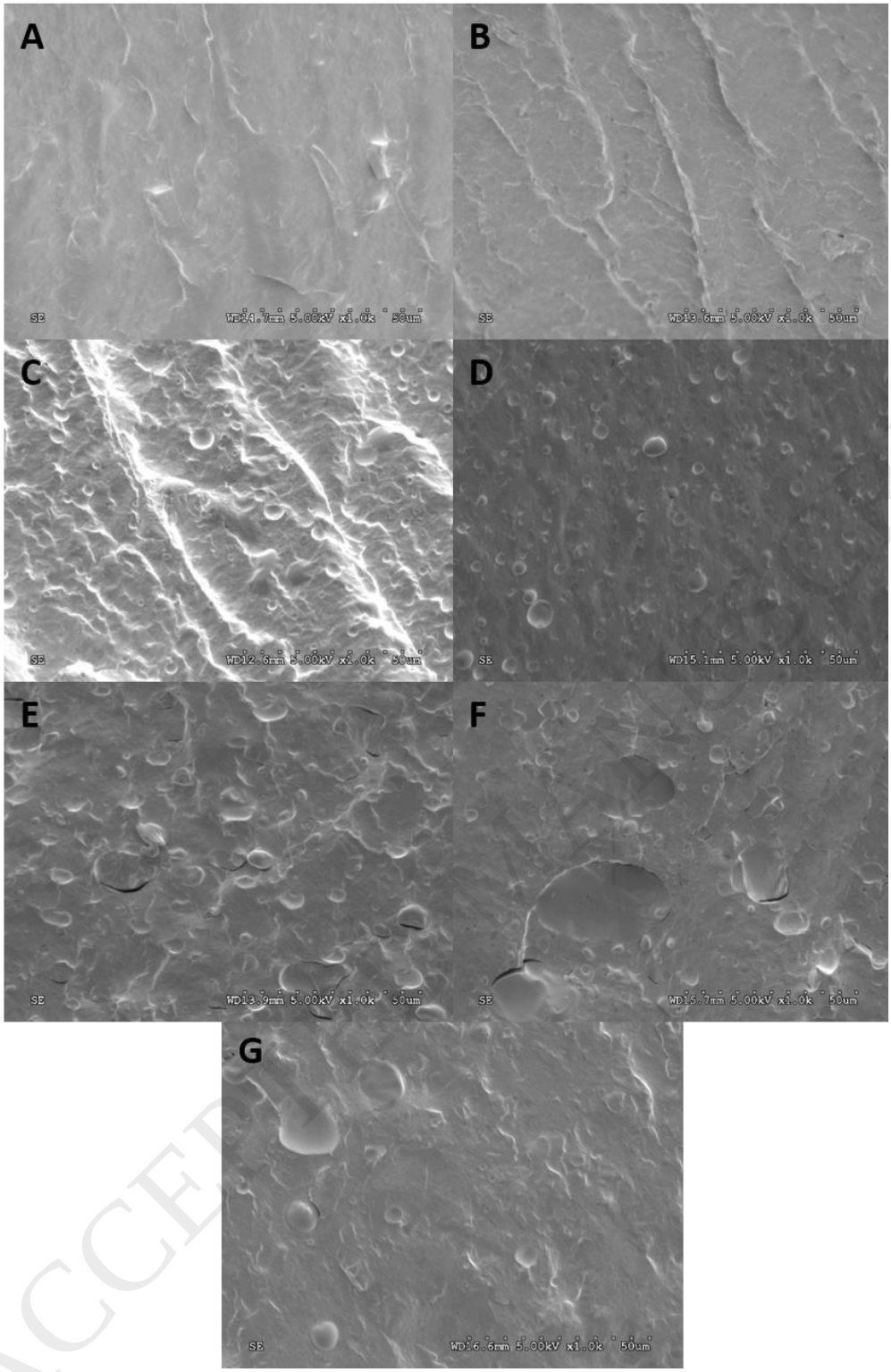

Figure 3. SEM micrograph of the cryogenic fracture surface of the samples. a) R0; b) R1; c) R5; d) R8; e) R10; f) R12; g) R15.

It is well known that dynamic mechanical properties provide valuable information concerning the structure and morphology of polymeric materials (Lopez et al., 2014).

Temperature sweeps at a constant frequency are shown in Figure 4. In general terms, the behavior observed is that expected according to the literature: loss tangent reflects two maxima corresponding to two different thermal transitions, as reported (Sreekumar et al., 2012); the first one, a temperature transition between -60 and -55 ºC corresponds to a glycerol-starch rich phase (Medina Jaramillo et al., 2015; Sreekumar et al., 2012; Lopez et al., 2014; López et al., 2011) while the second temperature transition, between -10 and 0 ºC (Figure 4a), is related to the molecular dynamics transition of the PVA-starch rich phase (Sreekumar et al., 2012).

Nevertheless, for those samples with a rosin content above 5% a third peak is readily noticed at around 40-50 ºC. The intensity of the peak tends to increase with the rosin content and at the same time is shifted to higher temperatures. This peak is logically associated to the rosin: at 5% rosin this peak is of low intensity and appears at around 30 ºC, at 8% the peak gains in importance and is shifted to 40 ºC and at higher rosin concentration the peak is still bigger but the peak temperature seems to remain unchanged, at around 50 ºC. These data, together with the SEM images and mechanical properties, suggest that above 8% rosin, it segregates into an immiscible phase (whose glass transition is at around 50 ºC) which shows poor compatibility with the continuous phase. At lower concentrations, a rosin-rich phase interacts with the rest of the components; these interactions provoke a decrease in the glass transition and have a reinforcement effect on the mechanical properties of the blend.

Frequency sweeps at 100 ºC were also performed since it was thought that complex viscosity profiles might increase our understanding of the processability of the blends studied since, in terms of the Cox-Merz´s rule, complex viscosity-frequency and

viscosity-shear rate profiles are equivalent. In addition, the idea was to elucidate likely miscibility by representations of the type of Cole-Cole plots (Li et al., 2016; Li et al., 2006).

Complex viscosity results as a function of frequency are given in Figure 5a. The starch/PVA samples with a rosin content lower than 8% behaved as typical non-Newtonian fluids that follows the power law over the whole tested frequency range, showing a marked decrease in viscosity as the rosin content increases. When the rosin content increases above 8%, a Newtonian plateau at low frequencies appears, but at 12 and 15% rosin the behavior is totally unexpected, and both formulations behave in a totally different way to the rest.

The Cole-Cole diagrams are shown in Figure 5b. In good agreement with the above results, it is possible to observe the smooth behavior in samples up to 8% rosin. Above this concentration, a more complex pattern is observed, revealing a lack of uniformity in the system and the existence of a multiphasic system which, in view of mechanical properties, seems to be immiscible.

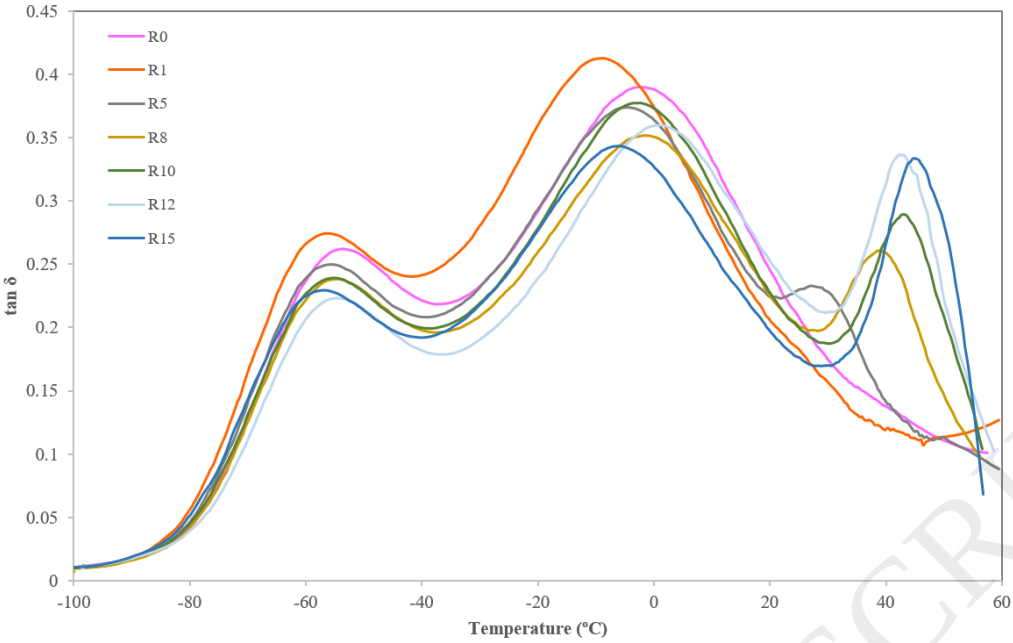

Figure 4. DMA spectra of the studied sheets. Dependence of Loss tangent (tan *δ*) on temperature at a constant frequency of 1 Hz.

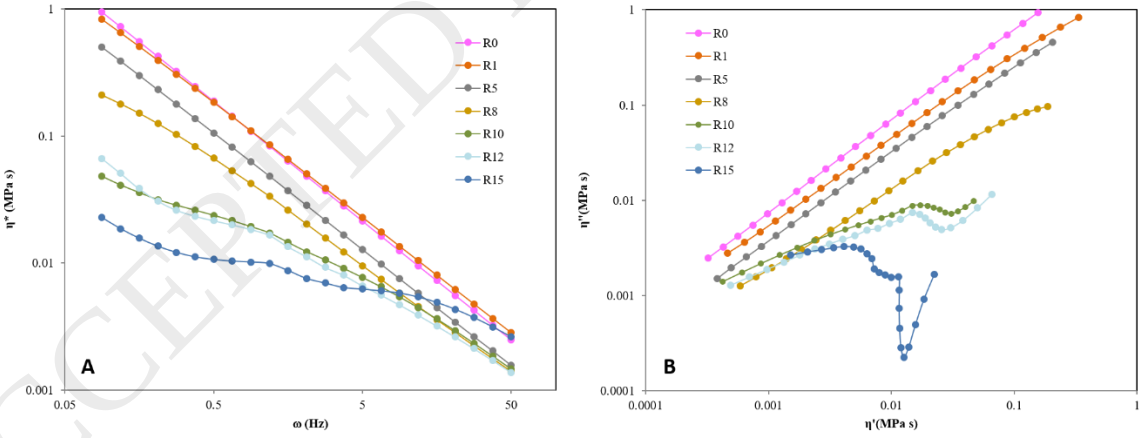

Figure 5. (a) Complex viscosity, η*, and (b) Cole-Cole diagram for the studied starch/PVA sheets.

4. Conclusion

Biodegradable starch/PVA blends containing rosin were successfully prepared by melt-mixing. This experimental procedure is comparatively cheaper and more scalable for industrial purposes than other processes, such as casting, to obtain sheets. The rosin content affects the mechanical properties of the blends significantly; the results obtained indicate that rosin is partially miscible with PVA/starch formulations, but at low concentrations its effect on processability (in terms of melt viscosity) and mechanical properties is positive. It is concluded that a rosin content of 8% achieves increases in maximum tensile strength and elongation at break of 72% and almost 400%, respectively, compared to the native starch/PVA blend. The results establish that formulations based on plasticized starch/PVA blends reinforced with rosin could be considered as interesting biodegradable materials for packaging applications.

Acknowledgements

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